

Surface modification of carbon-supported iron catalyst during the wet air oxidation of phenol: Influence on activity, selectivity and stability

Asunción Quintanilla^{b,*}, Nieves Menéndez^a, Jesús Tornero^{a,✕},
José A. Casas^b, Juan J. Rodríguez^b

^a *Departamento de Química Física Aplicada, Facultad de Ciencias Químicas, Universidad Autónoma de Madrid, Campus de Cantoblanco, 28049 Madrid, Spain*

^b *Area de Ingeniería Química, Facultad de Ciencias Químicas, Universidad Autónoma de Madrid, Campus de Cantoblanco, 28049 Madrid, Spain*

Received 19 October 2007; accepted 17 November 2007

Available online 5 December 2007

Abstract

Catalytic wet air oxidation (CWAO) of phenol with iron/activated carbon catalysts (Fe/AC) at temperature of 400 K and 8 atm of total pressure is an efficient treatment to oxidize a resistant pollutant such as phenol into biodegradable species, mainly short chain acids. Extended studies employing activated carbon catalysts point out significant changes in the carbon as a consequence of the CWAO process. After the long-term experiments carried out in this work it was concluded that these modifications consist of loss of microporosity, temporary decrease of the mesoporosity, decrease of the carbon/oxygen ratio on the catalyst surface, more acidic pH_{slurry} values, and aggregation of the α -Fe₂O₃ crystallites. The causes that provoke these changes and the reasons why they do not alter significantly the CWAO efficiency were analyzed. The way of exposition of Fe/AC catalyst to the reactants plays an important role in its activity and selectivity towards complete mineralization, namely oxidation to CO₂ and H₂O.

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Keywords: Activated carbon; Iron oxide; Wet oxidation; Mössbauer spectroscopy; Phenol

1. Introduction

Activated carbons have been widely used as adsorbent of organic and inorganic pollutants in order to clean waste streams (gas and liquid) coming from very different industrial sectors (food, pharmaceutical, chemical, petroleum, mining, automobile, etc.) [1]. Spent activated carbons have been usually regenerated by steam at high temperatures (1073–1123 K), treatment that increases the price of the overall process. In 1995, Levec and Pintar [2] published a study about the regeneration of activated carbons employing hot water at far lower temperatures (up to 200 °C) than thermal regenerations, avoiding the oxidation of activated carbon itself and abating the

desorbed pollutants by wet air oxidation [3]. As a consequence, activated carbon began to be tested as catalyst for wet air oxidation (WAO) process and literature started to appear in this field [4–10].

In the catalytic wet air oxidation process (CWAO), activated carbons have been used as catalyst and also as support. In the latter case, noble metals (Pt, Pd, Ru) have been tested [6,11,12] and in less extension, transition metals Cu, Fe, Ni, Co and Mo [13–16].

The employ of activated carbons as catalyst or support presents improvements comparing to catalysts based on transition and noble metals over conventional supports. For instance, in the CWAO of phenol, the most common pollutant chosen as target compound in the WAO studies, a higher phenol oxidation rate, a higher mineralization and therefore, a less toxic route is achieved [17,18].

However, when activated carbon is used in the CWAO process, significant changes in its textural properties have been

* Corresponding author. Tel.: +34 91 4972878; fax: +34 91 4973516.

E-mail address: asun.quintanilla@uam.es (A. Quintanilla).

✕ Deceased.

reported after a given time on stream [10,19,20]. Suarez-Ojeda et al. [10] studied the CWAQ of *o*-cresol, 2Cl-phenol and phenol at 5 g/L in aqueous solution with a commercial activated carbon at 413 K and 2 atm of oxygen in a trickle-bed reactor. In this study, the conversion and BET area of the catalyst after 72 h of time on stream were analyzed and it was found that the highest BET area reduction (98.4% with *o*-cresol, 91.7% with phenol and 88.6% with 2Cl-phenol) did not correspond to the highest pollutant conversion but to the susceptibility towards coupling reactions on activated carbon, quantified by the critical oxidation potential [21]. These coupling reactions take place mostly during the adsorption step and are stimulated in presence of O₂ and at high temperatures [22,23]. Santos et al. [19] also studied the CWAQ of different pollutants with a commercial activated carbon at 433 K and 16 atm of oxygen in a fixed-bed reactor. They also found a decrease in the BET area of the carbon after 120 h of time on stream (34% with *p*-cresol, 44% with *o*-cresol, 58% with *p*-nitrophenol and 35% with *o*-nitrophenol) and it was observed that, in phenol oxidation, that reduction was almost independent of the time on stream in the range of 80–200 h. The reduction of BET area was significantly lower than the observed by Suarez-Ojeda et al. [10] probably because of the different nature of the carbons and therefore, the different adsorption capacity. Quintanilla et al. [20] in the CWAQ of phenol with a commercial activated carbon in a trickle-bed reactor at 400 K and 8 atm total pressure found similar modifications than those given by Suarez-Ojeda et al. [10]. Quintanilla et al. [20] reported decreases of the BET area and the micropore volume of the activated carbon of 90% and 95%, respectively, after 64 h of time on stream. Also, the external area and mesoporosity were diminished. The amount of oxygen surface groups was also increased (CO₂ and CO desorbing upon TPD were multiplied by a factor of 8 and 3.5, respectively).

When iron is incorporated on the activated carbon a substantial increase of phenol and total organic carbon (TOC) conversion was observed. The former increased from 50% in presence of activated carbon to 95% with the carbon-supported iron catalyst and TOC conversion raised from 30% to 65%, both at a space time of 160 g_{CAT}-h/L. Also, the presence of Fe enhanced toxicity abatement at sufficiently high space time values [16,20]. This better performance of the carbon-supported iron catalyst is due to both the higher amount of oxygen surface groups, specially the more acidic ones, formed during the calcination process in the catalyst preparation, and the presence of the iron oxide itself since for a given amount of oxygen surface groups, higher conversions were obtained in presence of iron [20].

Moreover, the presence of iron stabilizes the activated carbon since a detrimental effect of wet oxidation on the porous structure of the activated carbons was observed [20]. A 40% reduction in BET area and a 30% in the micropore volume were observed after 216 h of time on stream, whereas the mesoporosity was not affected. The amount of oxygen surface groups was also increased but in less extension than in the activated carbon alone. CO₂ and CO desorbing upon TPD were double after 216 h of time on stream. These phenomena will be analyzed in detail in the present work.

The aim of this work is to study the physico-chemical stability of the carbon-supported iron catalyst (Fe/AC) through the WAO process. For this purpose, a long-term experiment was carried out to investigate the changes in the catalyst surface through time on stream. This experiment was conducted by putting in contact simultaneously the catalyst with the reactants, so that the catalytic bed was saturated in phenol in presence of oxygen (named as SOC experiments). The results have been compared to those found in a previous work [16] where the catalytic bed was first saturated in phenol in nitrogen atmosphere (named as SAC experiments). Therefore, the catalyst stability and activity have been also assessed by modifying the adsorption step (in oxygen or nitrogen atmosphere). The causes of the changes on the surface properties of the Fe/AC catalyst and their possible consequences in the CWAQ process have been also investigated.

2. Experimental

2.1. Preparation of the catalyst

A commercial hydrocarbon-derived activated carbon (AC) supplied by Merck (ref.: 102514) has been used as catalyst support in this study. It was previously sieved to a particle size in the range of 0.5–1 mm.

The catalyst was prepared by the incipient-wetness impregnation method employing an aqueous solution of Fe(NO₃)₃·9H₂O (Panreac) of the required concentration to obtain a Fe loading of 2.5 wt% with a solution volume exceeding by 10% the total pore volume of the support. Impregnation was followed by drying at room temperature for 2 h and overnight at 333 K. The catalyst was then heated up to 473 K within 2 h at two temperature rates (1 h at 0.67 K/min and 1 h at 1.67 K/min) and then calcined at 473 K during 4 h. Fe loading was determined by total reflection X-ray fluorescence spectroscopy (TXRF), using Si–Li detector in a TXRF Extra-II Rich & Seifert spectrometer.

2.2. Catalytic testing for phenol wet oxidation

Catalytic wet oxidation of phenol was conducted in a bench scale wet air oxidation unit with a trickle-bed reactor (TBR) operating in concurrent down-flow of both phases, liquid and gas. Detailed information about the components and operating procedure has been reported elsewhere [16].

Oxidation runs were performed by pumping an aqueous solution of 1000 mg/L of phenol at pH 3.5 (adjusted with H₂SO₄) to the reactor at different flow rates (0.125–2 mL/min) to cover a wide range of space time values (τ). Pure oxygen, continuously fed at 91.5 NmL/min, was used as oxidising agent. The reactor loaded with 2.5 g of catalyst was maintained at 400 K and 8 atm in all the experiments. The set of experiments were carried out by putting fresh catalyst in contact with phenol and oxygen without previous phenol saturation of the catalytic bed; therefore, adsorption and reaction processes take place simultaneously at different rates

until the steady state is reached. All the results presented correspond to steady state conditions.

Long-term experiments at $W/Q_L = 80 \text{ g}_{\text{CAT}}\cdot\text{h/L}$, $T = 400 \text{ K}$ and $P_T = 8 \text{ atm}$ were also carried out to study stability of the catalyst. Reactor was always loaded with 2.5 g of catalyst and the reaction was stopped at different times on stream for the catalyst.

The progress of the reactions was followed by taking periodically liquid samples from the reactor outlet. The liquid samples were analysed by different methods such as HPLC-diode array (Varian, mod. ProStar) and IC (Metrohm, mod. 761 Compact IC), to identify and quantify phenol and its reaction intermediates; TOC analyzer (O.I Analytical, model 1010 TOC analyzer) to determine the total organic carbon and TXRF (TXRF EXTRA II spectrometer) to measure Fe leached from the catalyst. The conditions have been fully described elsewhere [16].

2.3. Catalyst characterization

The porous structure of the fresh and used catalysts was characterized from the 77 K N_2 adsorption/desorption isotherms using an Onmisorp 100 CX apparatus. The micropore volume and the external surface area (non-micropore area, A_t) were obtained by the t-method. The mesopore volume was calculated as the difference between the volume of N_2 (as liquid) adsorbed at 0.95 relative pressure and the micropore volume. The morphology of the catalyst samples was observed by scanning electron microscopy (SEM) using a JEOL 5900 apparatus at an accelerating voltage of 20 kV.

Temperature-programmed desorption (TPD) was used to analyze the oxygen surface groups of the catalysts. TPD analyses were carried out as follows: a sample of 100 mg of carbon was placed in a quartz tube and was heated at 10 K/min up to 1173 K. A flow of 200 mL/min of He was continuously passed as carrier gas. The oxygen surface groups decompose and evolve as CO and CO_2 which were analyzed in a SIEMENS (mod. Ultramar 22) gas analyzer. The catalysts were also analysed for elemental composition, using a PerkinElmer Series II 2400 micro analyser.

The iron phase in the fresh and used catalysts was identified by Mössbauer spectroscopy and X-ray diffraction (XRD). Mössbauer spectra at room temperature and 77 K were recorded in triangle mode using a conventional spectrometer with $^{57}\text{Co}(\text{Rh})$ source. The spectra were analyzed by a non-linear fit using the NORMOS program [24] and the energy calibration was made using a $\alpha\text{-Fe}$ ($6 \mu\text{m}$) foil. X-ray powder diffraction patterns were acquired on a Siemens-D5000, operated in step-scan mode, with $\text{Cu K}\alpha$ (8.04 keV) radiation and a Si–Li detector provided by Kevex, cooled by Peltier effect that allows a resolution of 240 eV. Data were collected from 20° to 105° , at 0.02° and 40 s per step. Diffraction line profile analysis was performed by the program Diffac-AT (Analytical X-ray Systems). The mean crystallite size was determined from the line width by the Scherrer method.

The surface acidity of the carbons was characterized by measuring the pH of their aqueous suspensions according to the procedure described by Moreno-Castilla et al. [25].

3. Results and discussion

3.1. Characterization of the fresh catalyst

The BET and the external surface (A_t) areas as well as the pore volumes of the fresh Fe/AC catalyst are given in Table 1. These values show that the catalyst is essentially microporous and the contribution of mesoporosity represents close to a 10% of the BET area. The TPD curves are shown in Fig. 1 and the corresponding amounts of CO and CO_2 evolved are collected in Table 2. The peaks and shoulders of the TPD curves can be assigned to different functional groups depending on the temperature at which CO and CO_2 evolve [26,27]. To quantify the amount of the different oxygen surface groups, the TPD curves were deconvoluted by fitting each peak to a multiple Gaussian function. The numerical method employed was based on PEAKFIT 4.11. The results are collected in Table 3. As can be seen, the Fe/AC catalyst presents mainly carboxylic anhydride and carbonyl/quinone groups. The sharp peak centred around 940 K has been assigned to phenolic groups in Table 3, but looking at the shape of the CO profile may correspond in great part to CO resulting from reaction of Fe_2O_3 and C at that temperature. The pH slurry was 4.3 mainly due to carboxylic anhydride groups and also to the presence of iron [20].

The Mössbauer spectrum of the fresh catalyst is shown in Fig. 2. The spectrum consists in a broad quadrupole doublet indicating the absence of a long range magnetic ordering, which can be interpreted like the sum of two doublets with the same isomer shift ($\text{IS} = 0.355(1) \text{ mm/s}$) and different quadrupole splitting ($\text{QS} = 0.62(1) \text{ mm/s}$ and $\text{QS} = 1.04(1) \text{ mm/s}$, respectively). These values are typical for high spin Fe^{3+} and consistent

Table 1

Textural property of fresh and spent catalysts after different treatments ($W/Q_L = 80 \text{ g}_{\text{CAT}}\cdot\text{h/L}$)

Sample	tos (h)	S_{BET} (m^2/g)	A_t (m^2/g)	$V_{\text{micropore}}$ (cm^3/g)	V_{mesopore} (cm^3/g)
Fresh	0	890	72	0.393	0.101
SOC experiments					
SOC1	1	818	79	0.347	0.112
	29	408	68	0.161	0.099
SOC48	48	367	50	0.158	0.085
	60	536	68	0.241	0.099
	90	550	73	0.263	0.114
	133	597	83	0.306	0.124
SOC216	216	467	78	0.253	0.118
SAC experiments					
SAC0	0 ^a	678	82	0.284	0.119
SAC13	13	175	61	0.054	0.087
	37	136	54	0.040	0.083
	62	157	53	0.050	0.079
	134	384	74	0.151	0.108
SAC216	216	538	81	0.269	0.089
Acid water and N_2					
N25	25	976	89	0.377	0.138
Acid water and O_2					
O25	25	930	86	0.412	0.112

^a Saturated in phenol during 21 h under N_2 atmosphere.

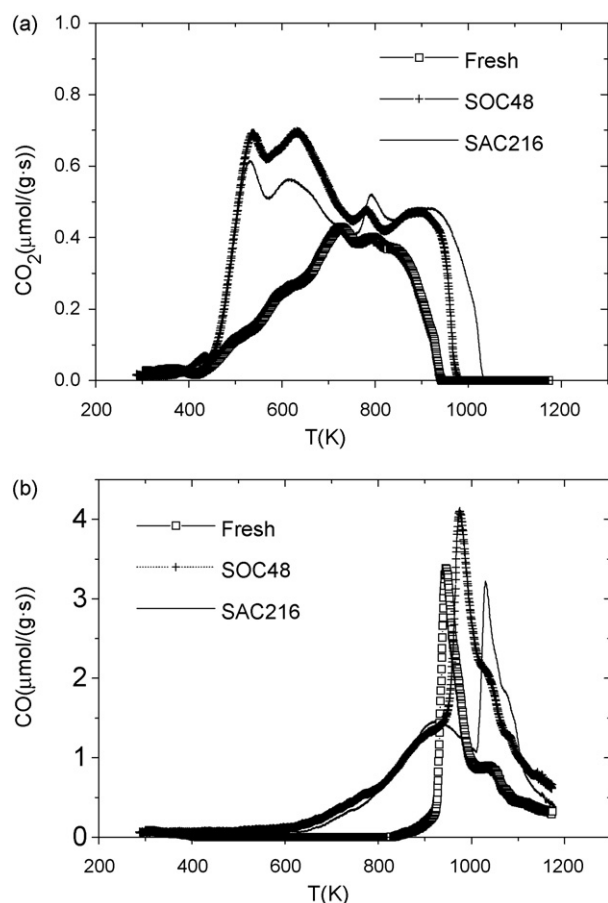


Fig. 1. TPD spectra of fresh and used catalysts after different times on stream. (a) CO evolution; (b) CO₂ evolution.

with values obtained for α -Fe₂O₃ nanoparticles (<7–4 nm); it is known that these spectral contributions are due to the core and the surface of the superparamagnetic oxide respectively [28,29]. Considering the size of the α -Fe₂O₃ nanoparticles, they must be located in the meso and macropores.

3.2. Catalytic behaviour

The results obtained in the experiments of CWAO of phenol in the TBR when the catalytic bed was saturated with phenol in oxic conditions (SOC) are shown in Fig. 3. In this figure, phenol and TOC conversions along with the normalized concentration of the intermediates (C_i/C_{Co}) are plotted vs. space time (W/Q_L). Results obtained in a previous work at the same operating conditions but with the catalytic bed saturated

Table 2

Amounts of CO and CO₂ released by TPD analysis and pH_{slurry} values for the fresh and spent catalysts

Sample	μmol CO/g carbon	μmol CO ₂ /g carbon	pH _{slurry}
Fresh	1714	841	4.30
SOC48	4357	1659	3.75
SAC216	3607	1659	3.77

with phenol in anoxic conditions (SAC), under N₂ atmosphere, before wet oxidation [16], have been also depicted. As can be observed, high phenol and TOC conversions were achieved at these mild temperature and pressure conditions with Fe/AC catalyst. The oxidation intermediates have been almost completely identified and quantified and no other significant peaks were detected in the samples exiting the reactor at the operating space time values. The TOC measured values and those calculated from the identified species differed in less than 5%, at most of the space time values tested. Comparing the results of these two set of experiments (SOC and SAC), it was found that in SOC conditions, when phenol and oxygen were simultaneously fed to the reactor without previous saturation of the catalytic bed, the conversion values for phenol and TOC were higher and also lower concentrations of intermediate species were detected. This higher TOC conversion must be due to the direct oxidation of phenol to CO₂ and H₂O (mineralization), rather than be caused by a faster breakdown of the cyclic intermediates (*p*-benzoquinone, hydroquinone and *p*-hydroxybenzoic acid) into short organic acids (mainly maleic, acetic and formic acids) and CO₂ because then the normalized concentration of acids (quite refractory at these operating conditions) in the SOC experiments should be higher than in SAC, which is not the case.

These results prove that the way phenol and oxygen are put in contact with the catalyst affects to its activity and selectivity. To analyze if the stability of the catalyst can also be affected, long-term experiments were conducted at $W/Q_L = 80$ g_{CAT}·h/L, $T = 400$ K and $P_T = 8$ atm after phenol saturation in SOC conditions. The results are presented in Fig. 4a, as phenol and TOC conversions vs. time on stream. A 9 day run was also carried out in a previous work [16] at the same operating conditions but after phenol saturation under N₂ atmosphere (SAC). These results are presented in Fig. 4b. Both figures (4a and b) show almost constant values of phenol and TOC conversions with time on stream. Thus, the stability of the Fe/AC catalyst is maintained, independently on the way of performing the pre-saturation step.

Table 3
Assessment of oxygen surface groups from deconvolution of TPD profiles

Sample	Groups evolved as CO ₂ (μmol/g)			Groups evolved as CO (μmol/g)		
	Carboxylic acid	Lactone	Carboxylic anhydride	Carboxylic anhydride	Phenol	Carbonyl/Quinone
Fresh	39	210	591	541	487	685
SOC48	234	793	632	523	754 + 501 (ether)	2579
SAC216	142	606	911	1143	866	1597

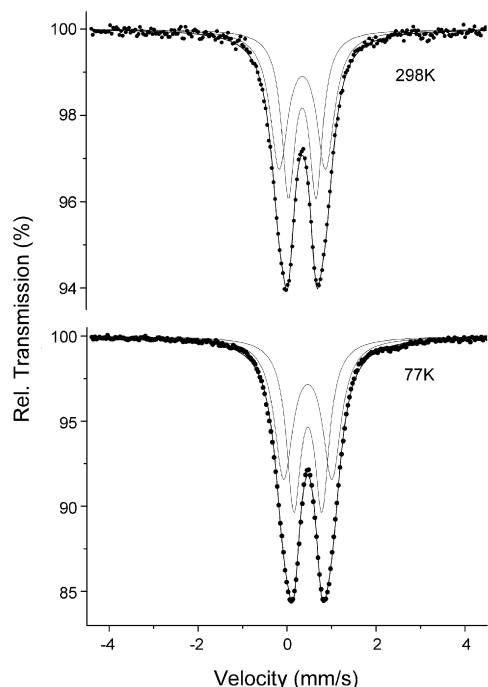


Fig. 2. Mössbauer spectra of fresh catalyst. The spectrum of the fresh catalyst was also recorded at ± 12.0 mm/s in order to leave out the existence of magnetically ordered α - Fe_2O_3 particles.

3.3. Physical and chemical modifications of the Fe/AC catalyst through CWAO

3.3.1. Changes in the carbon support

Evolution of the textural properties of the catalyst upon wet oxidation has been studied by obtaining the N_2 adsorption/desorption isotherms of the carbon catalyst after different times on stream. The results are given in Table 1. Also, two experiments were carried out in absence of phenol. Acid distilled water was continuously fed to the TBR during 25 h under N_2 or O_2 , at the same operating conditions than the CWAO experiments. The catalyst samples were labelled as N25 and O25, respectively. Their textural properties are collected also in Table 1.

From the values of Table 1, it can be seen that the wet oxidation process significantly modifies the textural properties of the catalyst by reducing mainly the BET surface area and the micropore volume. This must not be due to the operating conditions (see sample N25) neither to partial gasification of carbon by oxygen (see sample O25) but to adsorption of phenol, as shows sample SAC0, where only phenol in absence of oxygen has been passed through the bed. Moreover, the microporosity was more dramatically reduced when oxygen was also present, as proves the BET surface area value for sample SAC13, 85% lower than the fresh catalyst after 13 h of time on stream under oxidation conditions. The mesoporosity was also affected in some extent. This could be explained as the result of two different phenomena occurring simultaneously: (I) creation of new oxygen groups from oxidation of the carbon surface; these groups can be placed preferentially in the mouth of the micropores [30] and (II) formation of phenolic

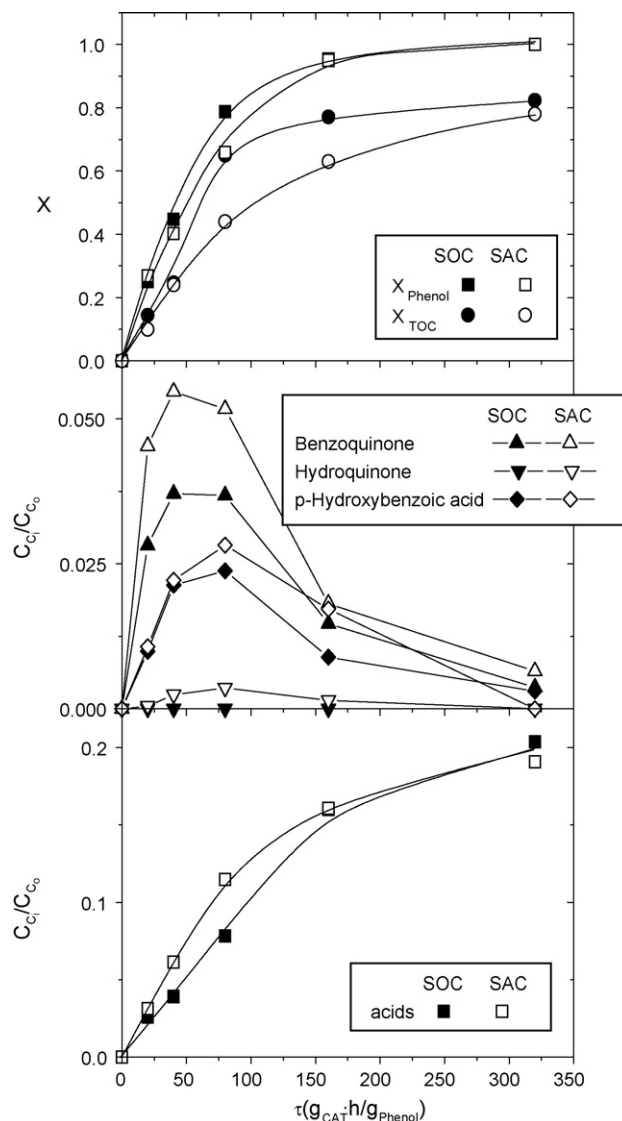


Fig. 3. Experimental results in the CWAO of phenol at 400 K and 8 atm of total pressure after catalytic bed saturation in oxic (close symbols) and anoxic (open symbols) conditions. $\text{pH}_0 = 3.5$, $C_{\text{Phenol},0} = 1000$ mg/L, $Q_G = 91.6$ NmL/min and $W = 2.5$ g.

condensation products on the activated carbon surface. The introduction of oxygen gives rise to oxidative coupling reactions leading to polymerization of phenol molecules [21–23].

Again, the way of putting in contact the three phases (phenol, oxygen and catalyst) marked a difference. In SOC conditions, after a time on stream of 13 h, a reduction up to 50% (calculated from SOC29) could be expected. Therefore, the condensation products were formed in less extension and were also more rapidly oxidized as proves the faster increase of the micro and mesoporosity through time on stream (Table 1). The higher availability of Fe not covered by a layer of phenol in SOC conditions can enhance the oxidation of the phenolic condensation products. A complete recovery of the textural structure of the carbon was never observed even after 216 h time on stream, which agrees with previous studies about phenolic condensation products remaining chemisorbed on the

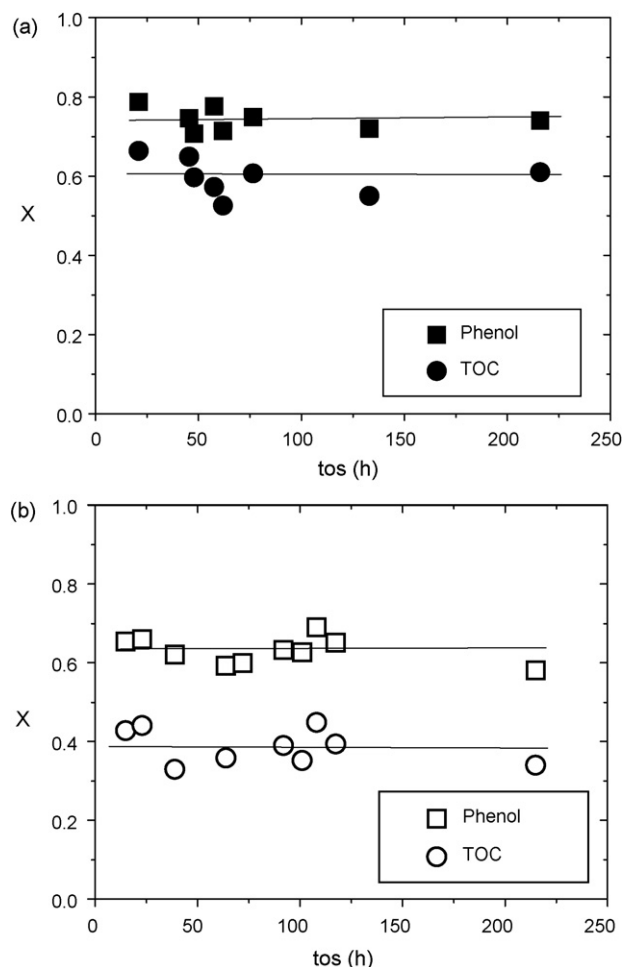


Fig. 4. Stability of the catalytic activity of the Fe/AC catalyst at 400 K, 8 atm of total pressure and $W/Q_L = 80 \text{ g}_{\text{CAT}}\cdot\text{h/L}$ after catalytic bed saturation (a) in oxic and (b) in anoxic conditions. $\text{pH}_0 = 3.5$, $C_{\text{Phenol},0} = 1000 \text{ mg/L}$, $Q_G = 91.6 \text{ NmL/min}$ and $W = 2.5 \text{ g}$.

activated carbon surface [21–23], but a steady state in terms of the amount of condensation products on the carbon surface seems to be reached as indicated by the almost constant value of BET area at high times on stream (when the rate of formation of those products may be similar to the rate of oxidation).

To gain evidence about the presence of such condensation products, an aliquot of spent catalyst was taken from the reactor and soaked in a basic solution (NaOH solution; pH 12). The liquid turned into a dark brown colour and after evaporation a blackish solid residue was obtained.

To confirm the oxidation of the carbon surface, elemental analyses of the catalysts after different times on stream were performed. The results, collected in Table 4 in a dry ash-free (d.a.f) basis, show that the C/O ratio decreases with time on stream which indicates the oxidation of the carbon itself simultaneously to the oxidation of the condensation products deposited on the carbon surface, as revealed, in this latter case, by the evolution of the BET area values (Table 1). These changes in the surface chemical composition affect to the $\text{pH}_{\text{slurry}}$ of the carbons (Table 3). The acidity of the catalysts was increased through the WAO process; therefore, the creation of the most acidic oxygen surface groups is expected. After

216 h of reaction, catalysts from SOC and SAC experiments reached a similar composition, but the time required to reach the steady state in the catalyst is shorter in SOC conditions.

To prove the presence of new acidic surface groups, TPD analyses were carried out for the SOC48 and SAC216 samples. The profiles are shown in Fig. 1. The amounts of CO and CO_2 evolved up to 1173 K were calculated and collected in Table 2. These results show a significant increase in the amount of oxygen surface groups of the catalysts after the CWAO process, as expected. The amounts of surface groups desorbed as CO and CO_2 in the spent catalysts were at least double with respect to the fresh one. Deconvolution of the TPD spectra leads to the assessment of oxygen groups given in Table 3. The results confirm that during the CWAO process important amounts of acidic groups, such as carboxylic acid, lactone and carboxylic anhydride are formed. A sharp peak appears again at high temperature in the CO profile, which can be due to CO resulting from reaction of Fe_2O_3 and C but also newly created phenolic and carbonyl/quinone groups. In the SOC48 sample, a new peak, assigned to ether was detected. These groups may come in part from the oxidation of both phenolic condensation products and carbon itself.

Catalyst samples at different times on stream were also analyzed by SEM. The micrographies of the fresh and used catalysts for the SOC experiments after 48 and 216 h time on stream (SOC48 and SOC216 samples, respectively) are shown in Fig. 5. It can be observed that the spent catalyst does not exhibit a polished surface as the fresh one. The SOC48 sample shows some residual deposits whereas the SOC216 presents a clearly attacked surface.

3.3.2. Changes in the metallic phase

The changes observed in the textural properties of the carbon support in the CWAO process can affect the dispersion of the metallic phase [32]. Thus, the nature and size of the Fe particles have been analyzed. The Mössbauer spectra of the catalyst after different times on stream for the SOC experiments are shown in Fig. 6. The main effect observed after the CWAO process is the evolution of the doublets characteristic of the fresh catalyst (Fig. 2) into a broad sextet. The better fit of the spectra at room temperature consists of two quadrupolar doublets, with hyperfine parameters fixed to the values of the fresh catalyst except their relative intensity, and one magnetic hyperfine field distribution, with parameters typical of small sized $\alpha\text{-Fe}_2\text{O}_3$. These latter parameters are listed in Table 5. The existence of a magnetic field distribution (represented by P vs. $H(T)$, included in Fig. 6) shows that the particle size is not uniform; however, the width of distribution decreases when increasing time of stream. In order to clarify the particle size, the spectra at 77 K were also obtained since at this temperature only the smaller particles will remain superparamagnetic.

These results are confirmed by XRD analyses (Fig. 7), where the characteristic reflections at $2\theta = 33.0$, 35.5 and 40.7° corresponding to $\alpha\text{-Fe}_2\text{O}_3$, which start appearing in the fresh sample over the activated carbon X-ray diffraction pattern, become more evident as the time on stream increases. The average $\alpha\text{-Fe}_2\text{O}_3$ particle size calculated by the Scherrer

Table 4
Results of elemental analyses^a (% d. a. f.)^b

tos (h)	C	H	N	S	O	C/O
0	80.20	1.03	0.65	0.66	14.97	5.36
SOC experiments						
1	62.00	2.66	0.51	0.58	31.72	1.95
216	56.50	2.74	0.44	0.27	37.55	1.50
SAC experiments						
13	73.80	2.21	0.50	0.46	20.5	3.6
62	71.60	2.20	0.44	0.43	22.87	3.13
134	67.60	2.40	0.45	0.32	26.83	2.52
216	54.00	2.70	0.53	0.37	40.27	1.34

^a Content of Fe: 2.5%.

^b Content of ash: 4%.

method is 32 nm for SOC48 and 40 nm for SOC216. The average hexagonal cell parameters of α -Fe₂O₃ calculated from the peaks in the high angle region were: $a = 5.039(1)$ Å and $c = 13.80(1)$ Å for SOC48, and $a = 5.041(1)$ Å and $c = 13.81(1)$ Å for SOC216, higher than the published values (JCPDS-No.33-0664). This indicates a significant formation of defects inherent to crystal growth *via* CWAO process. An increase of lattice parameters without structural changes would imply a decrease of the hyperfine magnetic field but, as shown in Table 5, the magnetic field increases slightly when increasing the particle size because this effect prevails over the previous one. Nevertheless the value of $H = 54T$ characteristic of bulk α -Fe₂O₃ at 77 K was not reached.

In order to explain the aggregation of α -Fe₂O₃, samples of catalysts obtained from the two 1 h runs carried out in absence of phenol with N₂ (N1) or O₂ (O1) gas fed, were also analyzed by Mössbauer. The superparamagnetic fractions were obtained from their spectra and the parameters are collected in Table 5. For sample N1, almost complete agglomeration of the iron oxide particles to bulk form occurred as in sample SAC0, whereas the sample O1 showed the same agglomeration as SOC1. These results prove that the operating temperature is the responsible of the growing of iron clusters on the activated carbon and the presence of O₂ delays this aggregation. This can be due to the interaction between O₂ and the α -Fe₂O₃ particles. It is known that the inclusion of Fe can increase the mobility of the reactive oxygen as has been already reported with the catalytic system Fe–Co-oxide [33].

In SOC conditions, the migration of Fe particles was triggered at the beginning of the reaction and went down at longer times on stream but always decreasing. The aggregation of Fe₂O₃ can contribute to the loss of carbon microporosity.

3.4. Influence of physical and chemical modifications on Fe/AC activity, selectivity and stability

As we have proved, the CWAO of phenol with carbon-based catalysts at mild operating conditions implies always physico-chemical modification of the activated carbon surface due to both the adsorbed phenolic condensation products and the formation of new oxygen surface groups as consequence of the oxidation of these condensation products and carbon itself. The

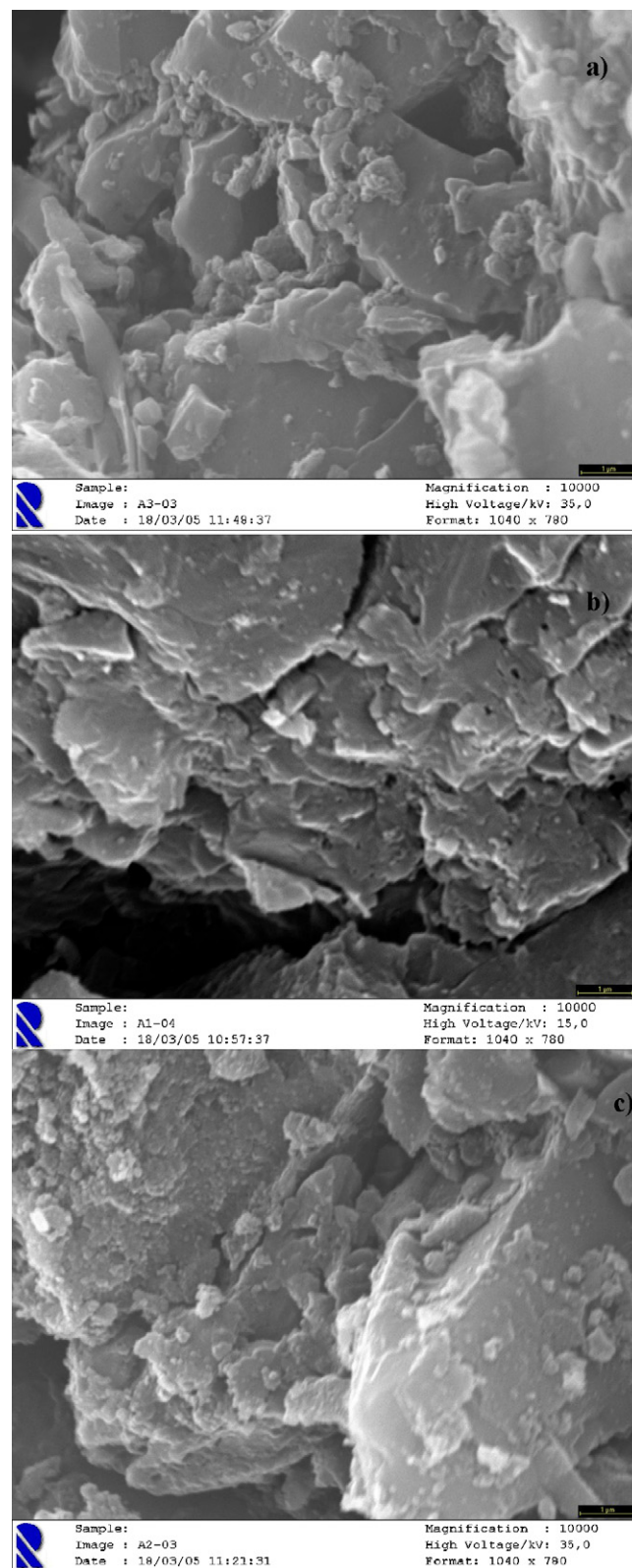


Fig. 5. SEM microographies for (a) fresh catalyst; (b) SOC48 and (c) SOC216 samples.

activity of Fe/AC in terms of phenol and TOC conversion was improved by saturation of the catalytic bed with phenol in oxygen atmosphere. In these conditions, condensations reactions were less favourable because the concentration of

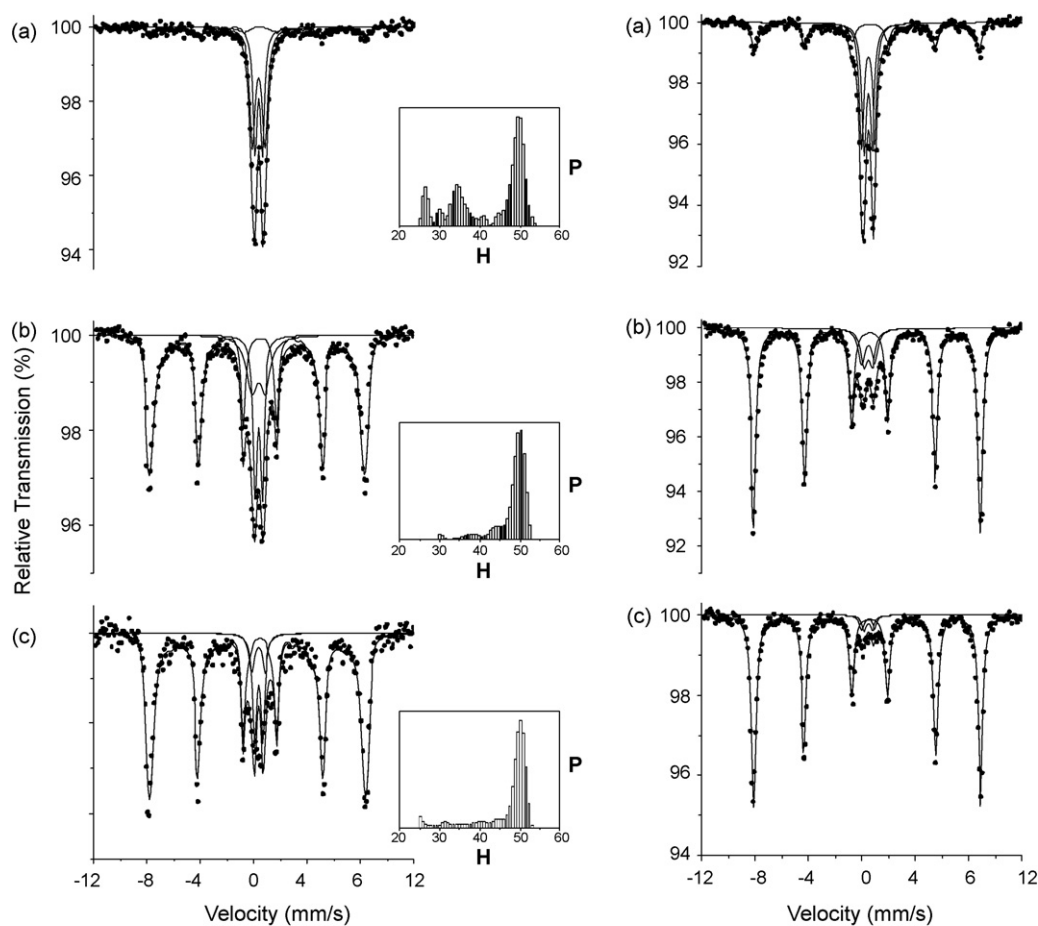


Fig. 6. Mössbauer spectra of used catalyst at room temperature (left) and 77 K (right); and different times of stream: (a) SOC1, (b) SOC48, (c) SOC216. Also is showing the hyperfine magnetic field distribution for these catalysts at room temperature (square).

Table 5
Mössbauer hyperfine parameters of catalyst samples

T (K)	Sample	IS ^a (mm/s)	QS (mm/s)	H (T)	%	% α -Fe ₂ O ₃ superparamagnetic
295 ^b	Fresh	0.355 (1)	0.62 (1)	—	47 (1)	100
		0.355 (1)	1.04 (1)	—	53 (1)	
	SAC0	0.37 (2)	−0.21 (2)	49.4 (4)	87 (1)	13 (1)
	SOC1	0.37 (2)	−0.22 (2)	47.5 (8)	16 (1)	84 (1)
	SOC48	0.37 (1)	−0.22 (2)	49.4 (2)	64 (1)	36 (1)
	SOC216	0.36 (1)	−0.21 (2)	49.4 (2)	81 (1)	19 (1)
	N1	0.37 (1)	−0.22 (2)	49.9 (2)	88 (1)	12 (1)
	O1	0.38 (3)	−0.23 (2)	49.3 (2)	10 (1)	90 (1)
77	Fresh	0.467 (1)	0.63 (1)	—	48 (1)	100
		0.467 (1)	1.08 (1)	—	52 (1)	
	SAC0	0.483 (2)	−0.22 (1)	53.2 (1)	97 (1)	3 (1)
	SOC1	0.487 (8)	−0.22 (2)	52.0 (1)	29 (1)	71 (1)
	SOC48	0.483 (2)	−0.22 (1)	52.5 (1)	83 (1)	17 (1)
	SOC216	0.483 (2)	−0.21 (1)	52.6 (1)	94 (1)	6 (1)
	N1	0.485 (2)	−0.21 (1)	52.7 (1)	96 (1)	4 (1)
	O1	0.491 (7)	−0.20 (1)	51.9 (1)	29 (1)	71 (1)

^a The isomer shifts are relative to α -Fe.

^b Average values for magnetic field distribution for used catalyst.

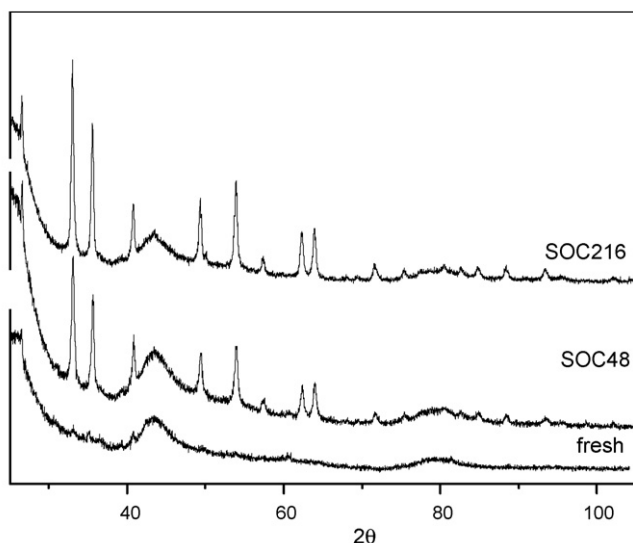


Fig. 7. X-ray diffraction pattern of fresh and used catalysts.

adsorbed phenol on the carbon surface is lower than when saturating the catalytic bed with phenol in absence of oxygen and also a higher concentration of O_2 can be expected since Fe is also more available. For these reasons, not only the activity but also the mineralization of phenol was favoured in SOC conditions and, therefore lower concentration of cyclic intermediates were present in the reactor effluent leading to a less ecotoxic wastewater [34].

The loss of microporosity does not affect significantly to the stability because the reaction takes place mostly on the meso and macropores. The temporary loss of mesoporosity, measured by the reduction of external area (A_t) seems not to be significant as to affect to the catalyst activity (external areas lower than $40 \text{ m}^2/\text{g}$ slightly decrease the activity in WAO of phenol [31]). The aggregation of Fe_2O_3 does not imply a change in the Fe/AC activity (Fig. 4), even when more than 90% of the Fe is present in clusters of about 40 nm (sample SOC216 in Table 5). Two reasons which are related can be addressed: (1) Fe on the carbon surface acts as a promoter; it favours the O_2 adsorption and (2) O_2 is not the limiting reactant at the operating conditions used in the experiments [35]. The new oxygen surface groups formed do not seem to enhance the activity as the original ones because otherwise the activity of the Fe/AC catalyst should be substantially increased.

4. Conclusions

During CWAO of phenol with Fe/activated carbon catalyst, physico-chemical properties of the Fe/AC are affected. The modifications of the activated carbon consist of significant loss of microporosity, temporary and slight decrease of the mesoporosity, decrease of the carbon/oxygen ratio and the pH_{slurry} values. They are caused by both (I) the formation of phenolic condensation products which with time on stream are oxidized although not completely, reaching a steady amount on the carbon surface; and (II) the oxidation of the carbon surface

itself giving rise to new acidic surface groups (mainly carboxylic acid, lactones and carboxylic anhydride). The modification of the metal phase consists in the aggregation of $\alpha\text{-Fe}_2\text{O}_3$ crystallites up to an average size of 40 nm due to the operating conditions. This sintering can also contribute to the loss of microporosity.

The way of exposition of Fe/AC catalyst to the reactants has an influence on the activity and selectivity of the catalyst because it affects the availability of Fe and, therefore, the concentration of oxygen on the catalyst surface. By putting simultaneously in contact the three phases (carbon–phenol–oxygen), the non-desirable condensation reactions are less favourable and higher phenol conversion and mineralization is obtained. These enhance of selectivity towards complete oxidation to CO_2 and H_2O leads to a less ecotoxic effluent.

In spite of the changes in the Fe/AC catalyst through the WAO process, a long-term constant activity was maintained because phenol oxidation occurs mainly on the meso and macropores, the new oxygen surface groups seems not to be as active as the original ones and because Fe acts as a promoter favouring the adsorption of O_2 .

Acknowledgements

Authors thank to Spanish MEC for the financial support through the project CTQ2004-02912/PPQ. Also we wish to thank to Dr. Eloisa Gonzalez-Serrano for her contribution to the characterization of the catalysts and the Servicio Interdepartamental de Investigación (SIDI) of Autonomía University of Madrid for the DRX and TXRF analyses.

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